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滇姜花中的新二萜成分——滇姜花素 D*

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摘要 从滇姜花 *Hedychium yunnanense* 根茎中分离到 3 个二萜成分, 分别为滇姜花 D (1), 圆瓣姜花素 A (2) 和 hedychenone (3), (1) 为新化合物, 其结构经波谱学方法鉴定为 13β - furanolabda - 6 - oxo - 7, 11 - dien - 17 - ol。

关键词 滇姜花, 滇姜花素 D, 二萜

分类号 Q 946

Yunnancoronarin D, A New Diterpenoid from *Hedychium yunnanense*

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Abstract Three diterpenoids, yunnancoronarin D (1), forrestin A (2), and hedychenone (3) were isolated from the rhizomes of *Hedychium yunnanense* Gagnep. The first one is a new compound and its structure was elucidated as 13 β - furanolabda - 6 - oxo - 7, 11 - dien - 17 - ol by spectra methods.

Key words *Hedychium yunnanense*, Yunnancoronarin D, Diterpenoid

We reported a series of antitumor diterpenoids from plants of *Hedychium yunnanense* (Zhao *et al*, 1995a; Zhao *et al*, 1995b; Zhao *et al*, 1996) and *H. forrestii* (Zhao *et al*, 1995c). Further study on the rhizomes of *Hedychium yunnanense* resulted in the isolation of three labdane type diterpenoids including a new one. In this paper we describe the structural elucidation of the compounds.

RESULTS AND DISCUSSION

Dried and pulverized rhizomes of *Hedychium yunnanens* collected in district of Guandu, Kun-

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ming, China, in 1993, were extracted with alcohol three times. The extract was further extracted with petroleum ether three times to give brown oil. Brown oil was purified by repeated column chromatography on silica gel and alumina to afford three diterpenes (1), (2) and (3).

Compound (1), colorless oil, $C_{20}H_{26}O_3$. The ^{13}C NMR spectrum gave 20 carbon signals, including one carbonyl (δ 200.1), eight olefinic carbons (CH×6, C×2), one hydroxymethyl carbon (δ 63.6). The ^1H NMR spectrum indicated the presence of a hydroxylmethyl (δ 4.03 and 4.12), a *trans* double bond (δ 5.69 and 6.35), and a β-substituted furan ring (δ 6.48, 7.34 and 7.39). The IR spectrum gave a sharp absorption band due to α, β-unsaturated ketone (1666 cm^{-1}), as well as a hydroxy (3418 cm^{-1}), gem dimethyl (1386, 1377, 1231 and 1160 cm^{-1}) and a furan (1507, 871 and 780 cm^{-1}).

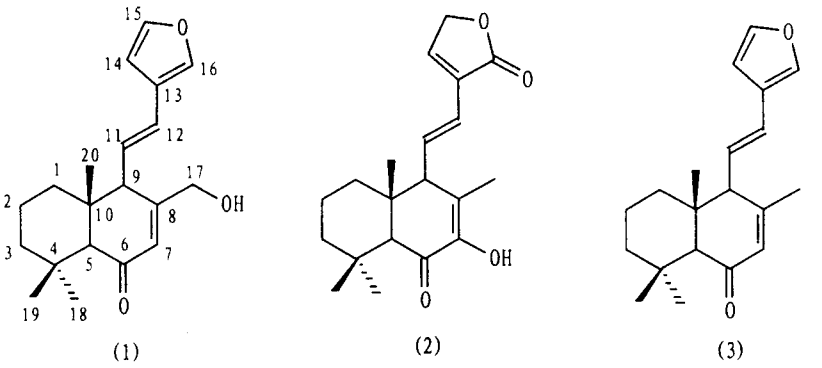
Table 1 ^{13}C NMR data of (1) ~ (3)

C	(1)	(2)	(3)	C	(1)	(2)	(3)
1	39.9	39.7	40.1	11	124.6	134.9	124.6
2	18.0	17.8	18.0	12	125.3	122.9	125.9
3	43.3	42.9	43.2	13	123.5	128.8	123.7
4	32.5	32.6	32.4	14	107.4	143.7	107.4
5	58.6	60.0	61.2	15	140.4	69.6	140.1
6	200.1	194.9	199.6	16	143.6	172.0	143.5
7	124.1	144.1	128.0	17	63.6	14.8	22.8
8	158.8	123.9	156.9	18	33.5	33.4	33.5
9	63.7	62.1	63.3	19	21.7	21.5	21.6
10	43.0	43.0	42.6	20	15.7	15.6	15.6

Table 2 ^{13}H NMR data of (1) ~ (3)

H	(1)	(2)	(3)
5	2.10 (1H, s)	2.09 (1H, s)	2.07 (1H, s)
7	6.09 (1H, s)		5.83 (1H, s)
9	2.98 (1H, d, 10.0)	2.88 (1H, d, 10.3)	2.89 (1H, d, 10.1)
11	5.69 (1H, dd, 10.0, 15.6)	6.65 (1H, dd, 10.3, 15.8)	5.74 (1H, dd, 10.1, 15.6)
12	6.35 (1H, d, 15.6)	6.22 (1H, d, 15.8)	6.34 (1H, d, 15.6)
14	6.48 (1H, s)	7.23 (1H, d, 2.04)	6.51 (1H, s)
15	7.34 (1H, s)	4.80 (2H, s)	7.35 (1H, s)
16	7.39 (1H, s)		7.40 (1H, s)
17a	4.12 (1H, d, 17.5)	1.68 (3H, s)	1.76 (3H, s)
17b	4.03 (1H, d, 17.5)		
18	0.94 (3H, s)	0.92 (3H, s)	0.94 (3H, s)
19	1.13 (3H, s)	1.10 (3H, s)	1.13 (3H, s)
20	1.16 (3H, s)	1.15 (3H, s)	1.16 (3H, s)

The ^{13}C and ^1H NMR spectra of 1 were similar to that of hedychenone (3) (Zhao *et al*, 1995a), indicating (1) was a labdane type furanoid diterpene. Comparision of ^{13}C NMR spectra of (1) and hedychenone suggested that C-17 of (1) was substituted by a hydroxyl group, which was also confirmedby the presence of hydroxylmethl (δ 4.03 and 4.12) in ^1H NMR spectrum. Thus the structure of (1) was elucidated to be 13 β-furanolabda-6-oxo-7, 11-dien-17-ol as shown



(1)　　(2)　　(3)

Fig.1　The structures of (1) ~ (3)

in Figure 1.

Compound (2) was identified as forrestin A, previously isolated from *H.forrestii* (Zhao et al, 1995c).

EXPERIMENT

General　Mps.uncorr. Optical rotations were recorded on SEPA - 300 with 2 cm cell. IR were taken with Perkin - Elmer 577. NMR were measured with AM - 400 spectrometer using TMS as the internal standard. FAB - MS were determined wit VG Autospec - 3000 mass spectrometer.

Extraction and isolation　The dried and pulverized rhizomes of *Hedychium yunnanens* (4.0 kg) collected in district of Guandu, Kunming, China, in 1993, were extracted with 95% EtOH three times at the refluex condition. The EtOH Extracts (410 g) was extracted with petroleum ether three times. Then the petroleum ether solutions were evaporated and got brown oil (230 g). The brown oil was separated into six fractions (Fr.A ~ F) by subjecting it to silica gel column chromatography (CC) using a petroleum ether - EtOAc gradient system. Fr.D was subjected to silica gel column chromatography eluting with petroleum ether - acetone (4:1) to give 518 mg of (2) as fine needles, together with a mixture. The mixture was further purified by alumina column chromatography eluting with $CHCl_3$ - EtOAc (4:1) to afford 31 mg of (1). Fr.A was recrystalized in cyclohexane - benzene (1:1) to give 8.2 g of (3) as needles.

Yunnancoronarin D (1) $C_{20}H_{26}O_3$, colorless oil, $[\alpha]_D^{20}$ + 76.42° (c, 0.265, $CHCl_3$). ν_{max}^{KBr} cm^{-1}: 3418, 1666, 1507, 1386, 1377, 1231, 1160, 871, 780. ^1H NMR and ^{13}C NMR: see Table 1 and 2.

Forrestin A (2) $C_{20}H_{26}O_4$, fine needles (benzene), mp is indefinite. ν_{max}^{KBr} cm^{-1}: 3400, 1743, 1665, 1640. ^1H NMR and ^{13}C NMR: see Table 1 and 2.

Hedychenone (3) $C_{20}H_{26}O_2$, needles (cyclohexane - benzene 1:1), mp 131.5 ~ 133℃. ν_{max}^{KBr} cm^{-1}: 1660, 1500, 870, 790. ^1H NMR and ^{13}C NMR: see Table 1 and 2.　(下转 259 页)

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